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An Evaluation of the Hewlett-Packard 5993B Gas Chromatograph-Mass Spectrometer

Environmental Monitoring and Support Lab.
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This report gives the results of an evaluation of a Hewlett-Packard Model 5993B computerized gas chromatograph/mass spectrometer. The evaluation was done according to the procedures found in EPA research report number EPA-600/4-80-025, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories." Changes in the "Performance Test" specifications for the BFB spectrum validation test have been made and are noted in the results for Tests 1 and 8. The system performed satisfactorily during the evaluation and is acceptable for the analyses of organic compounds using methods similar to EPA Methods 624 and 625. The HP-5993B system produced valid mass spectra, exhibited good to excellent stability, and gave a satisfactory detection limit. The precision and accuracy for external or internal quantitation using direct sample injection or purge and trap were excellent. Both 14 AMU and PBS mass spectral library searches were accurate; however, the search times using the PBS library search were longer than the requirements specified in the "Performance Tests." Some problems, particularly with brominated compounds, were discovered during this evaluation. The manufacturer corrected the instrument to alleviate these problems.

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AN EVALUATION OF THE HEWLETT-PACKARD 5993B GAS CHROMATOGRAPH/MASS SPECTROMETER

by

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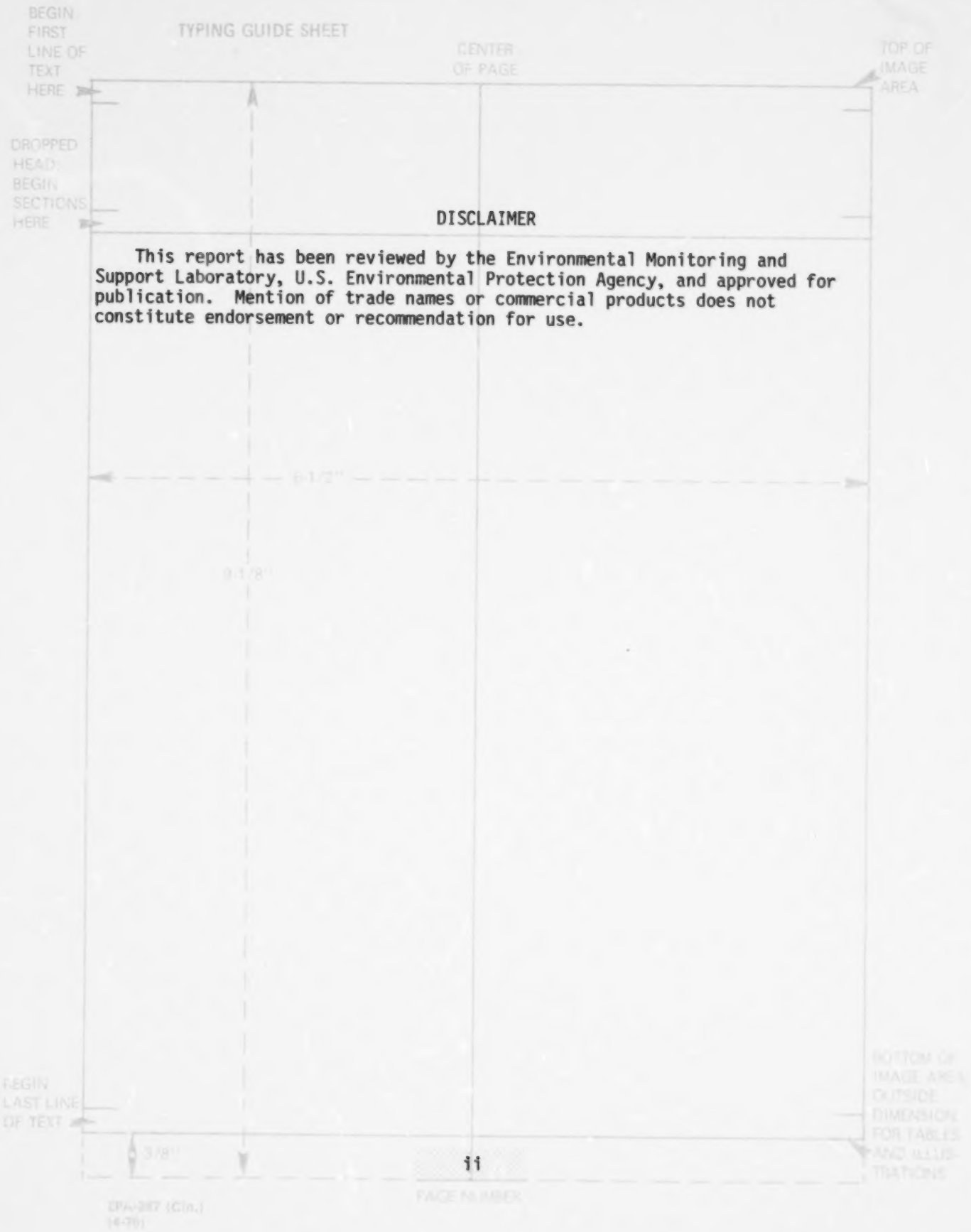

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report describes the application of a series of general purpose tests to evaluate the performance of the Hewlett-Packard Model 5993B gas chromatograph/mass spectrometer system. The report will be useful to the many Federal, State, local governments, and private laboratories that are presently performing or planning to perform environmental analyses using methods similar to the EPA approved Methods 624 and 625.

Robert L. Booth
Acting Director
Environmental Monitoring and Support Laboratory - Cincinnati

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ABSTRACT

This report gives the results of an evaluation of a Hewlett-Packard Model 5993B computerized gas chromatograph/mass spectrometer to determine its capabilities in performing environmental analyses. The evaluation was done according to the procedures found in EPA research report number EPA-600/4-80-025 entitled "Performance Tests for the Evaluation of Computerized Gas Chromatograhy/Mass Spectrometry Equipment and Laboratories." Some changes in the "Performance Test" specifications for the BFB spectrum validation test have been made and are noted in the results for Tests 1 and 8.

In general, the system performed satisfactorily during the evaluation and is acceptable for the analyses of organic compounds using methods similar to the EPA approved Methods 624 and 625. The HP-5993B system produced valid mass spectra, exhibited good to excellent stability, and gave a satisfactory detection limit. The precision and accuracy for external or internal quantitation using direct sample injection or purge and trap were well within the requirements specified in the "Performance Tests." Both 14 AMU and PBS mass spectral library searches were accurate; however, the search times using the PBS library search were longer than the requirements specified in the "Performance Tests." Some problems, particularly with brominated compounds, were discovered during this evaluation. The manufacturer corrected the instrument to alleviate these problems.

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SECTION 1

INTRODUCTION

This report details the results of an evaluation of a Hewlett-Packard Model 5993B (HP-5993B) computerized gas chromatograph/mass spectrometer (GC/MS). This system was evaluated using the procedures and tests specified in the EPA Report "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," (EPA-600/4-80-025). In Test 1, new BFB key ion abundances are presented. Some changes in the required purging efficiencies are noted in Test 8.

Eight of the ten tests were carried out to evaluate the actual performance of the HP-5993B regarding environmental analyses. Tests seven and ten were not conducted because the laboratory was not being evaluated and the HP-5593B did not have a solid probe inlet. The results of this evaluation apply only to the specific instrument on hand but can probably be considered valid for all HP-5993B systems operated under Revision C (or later) software. Revision A and Revision B software do not contain the CNORM software. Not all HP-5993Bs have the new DAC assembly. The following characteristics of the system were evaluated:

- ability to produce a valid mass spectrum
- day-to-day stability
- instrument detection limit
- ability to quickly recover from a saturated state
- precision and accuracy for identical analyses
- mass spectral library search
- precision and accuracy for inert gas purge and trap
- qualitative analysis with real samples

The system evaluated consisted of the following components:

1. HP-5992B Gas Chromatograph/Mass Spectrometer, electron ionization, mass range 1 to 800 amu.

2. HP-21 MX E Series Computer, 32K resident, operated under Revision C and Revision D 32K SIDS software,

3. HP-7900A Disc Drive, with one fixed and one removable disc; total storage of 5 megabytes,

4. HP-7970B Digital Tape Unit, 9-track tape,

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5. HP-2648A Graphics Terminal,

6. HP-7675A Purge and Trap Unit,

7. Tektronix 4532 Video Hard Copy Unit,

8. Zeta Research 100 Series Incremental Plotter.

9. Optional glass-lined jet separator.

Input to the system is accomplished using the CRT. Real-time output is directed to the CRT. Either the Tektronix hard copy unit or the Zeta research incremental plotter is used for making hard copy records of data. Data can be stored on either 9-track tape or on separate removable discs. A maximum of 256 discs can be cataloged at any one time.

On the HP-59938, acceptable mass spectrometer tuning is performed using the programs AUTOTUNE, OVERRIDE, and CNORM. AUTOTUNE automatically tunes the mass spectrometer to factory selected criteria using ions 69, 219, and 502 as perfluorotributylamine (PFTBA) is leaked into the analyzer section through a calibration valve. During tuning CNORM is off so that Part 2 of AUTOTUNE does not run. The program OVERRIDE allows the user to change the value of any parameter established by AUTOTUNE, particularly Mass Axis Gain, and store the new values in a separate tuning file if desired. CNORM is used to modify the raw abundances of ions in 80 amu wide windows to give mass spectra which meet all the relative abundance criteria for DFTPP (Table 1, Test 1).

The end result of using these three software programs is the ability to acquire mass spectra which achieve all the DFTPP key ion abundance criteria given in Table 1. This is demonstrated throughout this report and summarized in Table 3, Test 1.

The HP 59938 uses software rather than hardware to achieve acceptable abundance criteria. The use of software tuning in place of hardware tuning is, in general, acceptable. In the computer industry, it is widely recognized that either hardware or software can be used, interchangeably, to accomplish a specific task. The HP-59938 software tuning is interchangeable with hardware tuning; because once initiated, the software tuning is automatic and as permanent as hardware tuning and requires no further operator intervention. More extensive research concerning the use of software tuning is in progress and will be reported when completed.

SECTION 2

RESULTS OF THE EVALUATION

TEST 1 - SPECTRUM VALIDATION

This test is applicable to both decafluorotriphenylphosphine (DFTPP) and 4-bromofluorobenzene (BFB). The results obtained for both compounds are given. The tests were performed using the procedures found in Test 1 of the "Performance Tests."

Table 1 summarizes the key ion abundance criteria for decafluorotriphenylphosphine (DFTPP) as given in the "Performance Tests" and as suggested by Eichelberger, et al. (2). Examination of these criteria indicates that different types of instrumental performance are being evaluated with these criteria. The criteria for masses 51, 127, 198, 275, 365, and 442 check the performance of the mass spectrometer regarding mass calibration and relative abundance of ions in five discrete windows approximately 80 amu wide. The criteria for the mass pairs 69, 70; 197, 199; and 441, 443 check the resolution at masses where there is a significant contribution to A+1 and A-1 due to ^{13}C or the loss of ^{1}H.

Acceptable tuning is demonstrated by achieving all the DFTPP key ion abundance criteria listed in Table 1. On a HP-5993B system, this is accomplished in a two-step procedure. AUTOTUNE is run with CNORM off and 50 ng of DFTPP is injected through the GC inlet. The resolution criteria (69, 70; 197, 199; and 441, 443) are checked to determine if the criteria are achieved. Generally, AUTOTUNE gives acceptable resolution at the mass pairs 68, 70 and 197, 199 approximately 50% of the time. The resolution criteria for 441, 443 were always acceptable. If AUTOTUNE gives unacceptable resolution, the abundance of mass 68 being larger than 2% of mass 69 or the abundance of mass 199 being less than 5% of mass 198, OVERRIDE is used. If the parameter Mass Axis Gain is within tolerances, the value of the parameters AMU OFFSET or AMU GAIN are changed. When the abundance of mass 68 is too large, AMU OFFSET is increased by one increment and when the abundance of mass 199 is too small, AMU GAIN is increased by one increment. Sometimes both AMU GAIN and AMU OFFSET must be increased to achieve acceptable resolution. If Mass Axis Gain is out of tolerance (1.0000 ± 0.0005), the trimpot on the digital to analog converter is adjusted until Mass Axis Gain is within tolerances. Since the trimpot was added, no adjustment to AMU GAIN and AMU OFFSET have been necessary to achieve the resolution criteria.

The second step in achieving acceptable DFTPP key ion abundances on the HP-5993B involves using the program "Abundance Normalization System" (CNORM). As indicated above, acceptable resolution must be achieved using

TABLE 1

Decafluorotriphenylphosphine (DFTPP) Key Ion Abundance Criteria

MASS	CRITERIA
51	30% to 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 to 60% of mass 198
197	< 1% of mass 198
198	Base Peak, 100% relative abundance
199	5 to 9% of mass 198
275	10 to 30% of mass 198
365	> 1% of mass 198
441	present and < mass 443
442	> 40% of mass 198
443	17 to 23% of mass 442

AUTOTUNE and OVERRIDE. The relative abundance criteria for DFTPP (masses 51, 127, 198, 275, 365, and 442) are never fully achieved using the tuning parameters established by AUTOTUNE. In the shorter mass range for BFB, the relative abundance criteria were always achieved. CNORM is used to modify the raw abundances of ions in the 80 amu wide windows to give mass spectra which meet all the relative abundance criteria for DFTPP. Table 2 summarizes a typical second step using the program CNORM. The relative abundance of the key ions in a background corrected mass spectra of 50 ng of DFTPP is given in Table 2 relative to both base peak (442=100%) and to mass 198 before CNORM is applied. The relative abundance in the lower end of the mass spectrum of DFTPP is low compared to the key ion abundance criteria and is high in the high end. All resolution criteria are achieved before using CNORM. CNORM is run and the background subtracted relative abundance at ions 51, 127, 198, 275, and 442 (column 2, Table 2) is entered at the proper prompts. The program generates a file which is stored and then applied to the original data file to produce an adjusted data file. The adjusting file is automatically applied to all subsequent data. No further operator intervention is needed. The net result is summarized in the last column of Table 2, all DFTPP key ion abundance criteria are achieved. The adjustment is done using division with all divisors greater than one. CNORM warns the operator if any divisor is larger than 8. No ion abundance will disappear after CNORM adjustment if the raw ion abundance is greater than the divisor. Also, no ion abundance will saturate, because the divisors are always larger than 1.

Typically, a daily system check takes 10 to 20 minutes to perform. Two minutes are needed to run AUTOTUNE, five minutes to obtain a background corrected mass spectra of 50 ng of DFTPP, five more minutes to obtain a second mass spectrum of 50 ng of DFTPP if OVERRIDE must be used, and another five minutes to generate a CNORM file.

DFTPP

A glass column 1.8 m x 2 mm ID packed with 3% OV-17 on 80/100 Chromosorb W AW DMCS was used.

GC CONDITIONS: Oven, 200°C; Injector Port, 250°C; Carrier gas, helium at 30 mL per minute.

MS CONDITIONS: Repetitive scans from 40 to 450 amu; 3.8 seconds per scan (A/D=6); and a threshold of 5. AMU OFFSET is three digital units larger than last AUTOTUNE result and EM voltage was raised 200 volts.

CNORM FILE: Obtained from the raw data file (10014) and applied after acquisition.

The retention time of DFTPP was 3.8 minutes (21 scans). The background corrected mass spectra, after CNORM, is given in Figure 1. The spectrum shown (20-17) was selected according to the instructions given in the "Performance Tests" which indicate selection of a spectrum on the front side of the peak as close to the apex as possible and subtracting a spectrum just prior to the start of the peak. In general, the spectrum selected (20) is

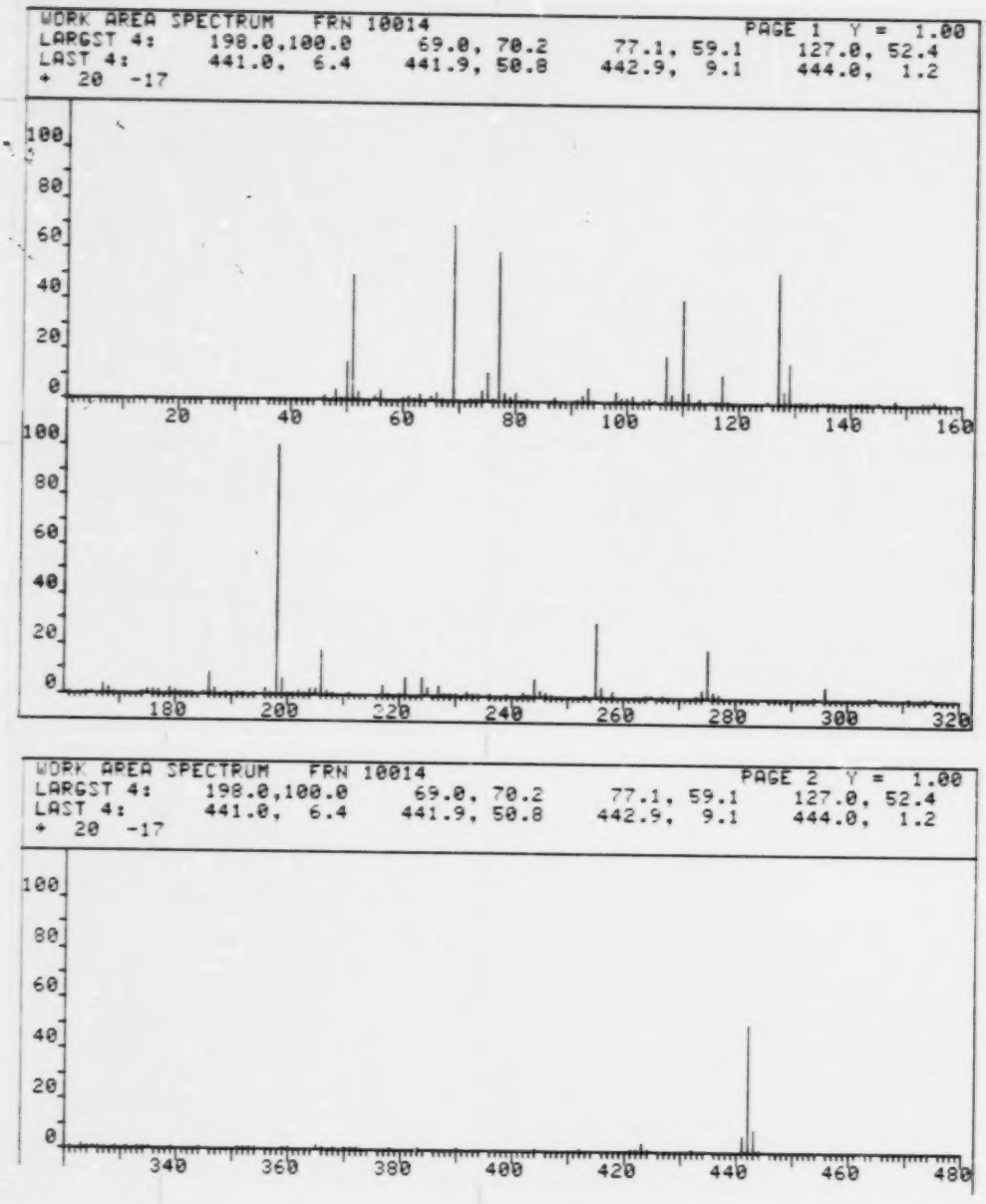

Figure 1. Mass spectrum of 50 ng of DFTPP, 0 hours, test 1.

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the spectrum which contains the maximum abundance of mass 442 which usually occurs one scan prior to the apex of the peak shown in the Total Ion Current Profile.

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TABLE 2

Comparison of DFTPP Key Ions Before and After Application of CNORM

MASS	Relative Abundance Before CNORM Base Peak=442 442=100%	198=100%	Relative Abundance After CNORM Base Peak=198
51	6.7	19.0[a]	45.3 (45.0)[c]
68	0.0	0.0	0.0
70	0.0	0.0	0.0
127	9.2	26[a]	50 (50)[c]
197	0.0	0.0	0.0
198	34.7	100	100 (100)[c]
199	2	5.7	5.8
275	11.1	32.0[b]	19.7 (20)[c]
365	2.4	6.9	1.1
441	11.8	34.0	6.9
442	100.0	288[b]	59.3 (60)[c]
443	18.5	53.3	10.4

a - Relative abundance too small
b - Relative abundance too large
c - CNORM Target Value

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Table 3 summarizes the DFTPP key ion abundances for spectrum validation as obtained on the HP-5993B over a 42 day period. Acceptable performance was always achieved after CNORM was used. The HP-5993B meets all the DFTPP key ion abundance criteria and will produce valid mass spectra which will be similar, if not identical, to spectra in collections and textbooks which have been gathered over the years on other types of mass spectrometers.

BFB

A glass column 1.8 m x 2 mm ID packed with 1% SP-1000 on 60/80 mesh Carbopak B was used.

GC CONDITIONS: Oven, 240°C; Injector Port, 150°C; Carrier gas, helium at 30 mL per minute. The oven is set above the maximum temperature recommended for this column to elute BFB in a short period of time. Keep excursions above 225°C to a minimum to prolong the life of the GC column.

MS CONDITIONS: Repetitive scans from 20 to 220 amu; 4.0 seconds per scan (AD=13); use of OVERRIDE was not necessary in this case.

CNORM FILE: CNORM was not required to produce valid mass spectra for BFB since the mass range was 20 to 220 amu.

The retention time of BFB was 5.6 minutes (27 scans). The BFB key ion abundance criteria, which has been updated since publication of the "Performance Tests" are given in Table 4. The criterion for the relative abundance of mass 50 was changed from 20 to 40%, to 15 to 40% of the base peak and that for mass 75 was changed from 50 to 70%, to 30 to 60% of the base peak. The resolution criterion for mass 173 was changed from less than 1% of mass 95 to less than 2% of mass 174. The criterion for mass 176 has been changed; namely, the acceptable range for the abundance of mass 176 divided by the abundance of mass 174 is now between 0.95 and 1.01. The resolution criteria for DFTPP are based on mass pairs containing significant contributions due to ^{13}C and the loss of ^{1}H. In the case of BFB, there is a significant contribution to an A+2 ion due to the presence of ^{81}Br and the criterion for mass 176 now reflects this. The HP-5993B achieves all the abundance criteria for BFB. CNORM is not needed to achieve the criteria when using BFB.

Table 5 summarizes the BFB key ion abundance criteria for spectrum validation as obtained on the HP-5993B before repair by factory personnel. Inspection of the table indicates that acceptable performance for all criterion except the ratio 176/174 can be achieved at the beginning of the day. During the course of a day, after acquisition of about 2000 spectra (4 half-hour runs), the ratio 176/174 gets worse with respect to the acceptable range of 0.95 to 1.01. Once the ratio 173/174 exceeded the acceptable limit of less than 2%. This is disturbing because it indicates that the resolution parameters AMU OFFSET and AMU GAIN would have to be updated halfway through the working day to maintain acceptable resolution for those ions containing bromine. This was not the case when DFTPP was used for spectrum validation, resolution remained stable throughout the day.

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TABLE 3

Summary of DFTPP Spectrum Validation Tests
Obtained with the HP-5993B

	ABUNDANCE CRITERIA						CHANGES FROM AUTOTUNE PARAMETERS	
FILE	m/e 51 30-60%	m/e 127 40-60%	m/e 198 100%	m/e 275 10-30%	m/e 365 > 1%	m/e 442 > 40%	AMU OFFSET	AMU GAIN
10003	46.4	56.9	100.0	21.7	1.4	48.3	+1	+1
10004	45.0	50.0	100.0	19.8	1.5	60.5	0	0
10010	41.4	58.5	100.0	20.3	1.9	79.6	+1	+1
10014	50.0	52.4	100.0	19.4	1.6	50.8	+3	0
10016	47.0	48.0	100.0	19.6	1.1	45.9	+3	0
10030	44.8	52.3	100.0	19.9	1.8	59.8	0	0
10034	38.8	52.0	100.0	20.8	1.6	69.6	0	0
10042	36.5	46.0	100.0	22.5	1.6	88.4	0	0
10052	42.7	47.9	100.0	22.3	1.4	73.9	0	0
10054	37.0	48.7	100.0	18.7	1.3	53.8	0	0
10063	45.3	50.0	100.0	19.3	1.1	59.3	+2	0
10071	45.0	50.6	100.0	20.3	1.2	59.2	0	0
10101	45.0	50.0	100.0	20.0	2.3	59.7	+1	0
10112	45.1	50.1	100.0	20.0	2.3	60.0	+1	0
Mean	43.6	51.0	100	20.3	1.58	62.1		
Std Dev	3.88	3.38	-	1.13	0.387	12.0		
RSD (%)	8.90	6.63	-	5.57	22.6	19.3		

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TABLE 3 (Continued)

Summary of DFTPP Spectrum Validation Tests
Obtained with the HP-5993B

	RESOLUTION CRITERIA					
FILE	68/69 < 0.02	70/69 < 0.02	197/198 < 0.01	199/198 0.05-0.09	441/443 > 0 & > 1	443/442 0.17-0.23
10003	0.000	0.000	0.007	0.059	0.651	0.178
10004	0.000	0.000	0.000	0.055	0.612	0.200
10010	0.011	0.000	0.000	0.061	0.580	0.173
10014	0.000	0.000	0.004	0.060	0.703	0.179
10016	0.011	0.000	0.000	0.059	0.613	0.203
10030	0.004	0.000	0.000	0.060	0.592	0.209
10034	0.019	0.000	0.004	0.052	0.625	0.184
10042	0.005	0.017	0.005	0.055	0.623	0.189
10052	0.000	0.000	0.000	0.059	0.667	0.195
10054	0.005	0.004	0.008	0.059	0.649	0.180
10063	0.000	0.000	0.000	0.058	0.663	0.175
10071	0.000	0.017	0.000	0.061	0.644	0.176
10101	0.017	0.000	0.000	0.055	0.693	0.191
10112	0.000	0.000	0.000	0.056	0.676	0.185
Mean	0.00586	0.00271	0.00200	0.0576	0.642	0.187
Std Dev	0.00722	0.00614	0.00296	0.00271	0.0366	0.0113
RSD(%)	123	226	148	4.70	5.70	6.04

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The mass spectrum of 4-bromobiphenyl in Test 4 gave a $^{81}Br/^{79}Br$ ratio of 0.96% when DFTPP was used for spectrum validation. Also, in those cases when AUTOTUNE returned parameters that did not give acceptable resolution for the BFB key ions, AMU OFFSET had to be lowered and AMU GAIN had to be raised to achieve acceptable resolution. When DFTPP was used for spectrum validation, and AUTOTUNE did not return parameters giving acceptable resolution, both AMU OFFSET and AMU GAIN had to be raised to achieve acceptable resolution.

TABLE 4

4-Bromofluorobenzene (BFB) Key Ion Abundance Criteria

MASS	CRITERIA
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% relative abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but > 101% of mass 174
177	5 to 9% of mass 176

Hewlett-Packard identified the source of this resolution problem for brominated compounds and replaced certain items in the mass spectrometer. A digital-to-analog converter (DAC) and a center wrapped shielded cable were replaced. The unacceptable resolution was occurring because abundance was not being reported at the centroid of the peak. The new DAC contains a trimpot which is used to adjust Mass Axis Gain to within a tolerance of 1.0000 ± 0.0005. This specification ensures that abundance is reported at the centroid of the peak. The OVERRIDE report on Figure 2, obtained before the DAC was replaced, shows Mass Axis Gain equal to 1.00267. This would now be out of tolerance, but since DFTPP does not contain strong A+2 ions, no resolution problems were evident.

Table 6 summarizes BFB validation tests obtained since the DAC was replaced. All resolution criteria are routinely achieved. There were 16 half-hour runs (9800 spectra) obtained between the validation tests at files 10503 and 10520 and all validation tests were achieved. Obviously, there is no longer a decay in resolution over a short period of time.

In summary, the HP-5993B can achieve acceptable spectrum validation using either DFTPP or BFB.

TABLE 5

Summary of BFB Spectrum Validation Tests
Obtained With the HP-55993B Before DAC Replacement

		ABUNDANCE CRITERIA				CHANGES FROM AUTOTUNE PARAMETERS	
FILE		m/e 50 15-40%	m/e 75 30-60%	m/e 95 100%	m/e 174 > 50%	AMU OFFSET	AMU GAIN
10159	a	16.9	45.5	100	89.7	0	0
10120	a	20.0	38.4	100	90.1	0	0
10123	b	16.9	43.2	100	85.5	0	0
10124	b	17.7	43.1	100	89.4	0	0
10125	b	16.1	45.1	100	84.8	0	0
10126	b	15.8	44.1	100	95.5	0	0
10127	b	17.2	46.4	100	92.8	0	0
10128	b	18.1	47.6	100	83.2	0	0
10129	b	16.5	41.1	100	93.2	0	0
10138	a	20.8	44.9	100	75.5	+1	-2
10139	b	17.8	44.5	100	77.4	+1	-2
10140	c	18.4	44.1	100	76.8	+1	-2
10141	c	20.2	48.1	100	76.1	+1	-2
10142	c	19.6	42.4	100	83.8	+1	-2
10143	b	19.1	44.0	100	79.7	+1	-2
10145	a	16.9	44.6	100	81.6	+1	-1
10146	b	20.3	45.9	100	74.6	+1	-1
10147	c	18.0	44.4	100	70.0	+1	-1
10148	c	19.6	46.5	100	68.0	+1	-1
10149	c	16.5	42.2	100	86.4	+1	-1
10150	b	19.3	46.8	100	77.9	+1	-1
10151	c	19.6	46.1	100	77.9	+1	-1
10152	c	18.5	48.1	100	73.9	+1	-1
10153	c	20.0	48.5	100	69.5	+1	-1
10154	b	17.8	50.1	100	70.8	+1	-1
10160	a	21.4	46.2	100	66.3	0	0
10161	c	18.8	42.7	100	68.7	0	0
10162	c	21.6	45.7	100	75.2	0	0
10163	c	20.4	48.0	100	74.8	0	0
Mean		18.6	45.1	100	79.6		
Std Dev		1.63	2.49	-	8.26		
RSD (%)		8.76	5.52	-	10.4		

a daily system check
b 30 minute run, Septum Injection
c 30 minute run, Purge and Trap

TABLE 5 (Continued)

Summary of BFB Spectrum Validation Tests
Obtained With the HP-55993B Before DAC Replacement

		RESOLUTION CRITERIA				
FILE		96/95 .05-.09	173/174 < .02	175/174 .05-.09	177/176 .05-.09	176/174 .05-1.01
10159	a	.069	.000	.0847	.0506	0.948*
10120	a	.052	.000	.0666	.0589	0.980
10123	b	.089	.000	.0795	.0705	0.946*
10124	b	.071	.000	.0772	.0721	0.915*
10125	b	.078	.000	.0837	.0894	0.936*
10126	b	.073	.000	.764	.0832	0.918*
10127	b	.074	.000	.0862	.0688	0.877*
10128	b	.078	.000	.0817	.0734	0.917*
10129	b	.075	.016	.0826	.0853	0.868*
10138	a	.074	.000	.0636	.0615	0.948*
10139	b	.071	.000	.0814	.0641	0.928*
10140	c	.084	.021*	.0768	.0545	0.956
10141	c	.069	.000	.0828	.017	0.949*
10142	c	.072	.000	.0847	.0893	0.949*
10143	b	.074	.000	.0753	.0840	0.926*
10145	a	.061	.000	.0723	.0545	0.967
10146	b	.072	.000	.0885	.0542	0.964
10147	c	.074	.000	.0871	.0852	0.956
10148	c	.063	.000	.0824	.0886	0.979
10149	c	.087	.000	.0741	.0757	0.872*
10151	b	.084	.000	.0783	.0894	0.905*
10151	c	.076	.000	.0809	.0784	0.868*
10152	c	.072	.000	.0787	.0824	0.840*
10153	c	.070	.000	.0806	.0817	0.898*
10154	b	.068	.000	.0791	.0885	0.814*
10160	a	.066	.000	.0890	.0662	0.956
10161	c	.073	.000	.0640	.0875	0.965
10162	c	.077	.000	.0851	.0879	0.968
10163	c	.076	.000	.0842	.0781	0.908*
Mean		0.0732	.00107	0.0796	0.0754	0.925
Std Dev		0.00755	.00400	0.00661	0.0125	0.0427
RSD (%)		10.3	394	8.30	16.6	4.61

*Does not meet criterion
a Daily system check
b 30 minute run, Septun Injection
c 30 minute run, Purge and Trap

TABLE 6

Summary of BFB Spectrum Validation Tests
Obtained with the HP-5993B after DAC Replacement

	Abundance Criteria				Changes from Autotune Parameters	
FILE	m/e 50 15-40%	m/e 75 30-60%	m/e 95 100%	m/e 174 > 50%	AMU OFFSET	AMU GAIN
20004	17.8	39.1	100	93.5	0	0
20008	20.2	41.8	100	94.6	0	0
10496	19.8	41.9	100	76.4	0	0
10503	19.4	41.3	100	96.1	0	0
10520	21.0	41.8	100	79.4	0	0
10526	23.9	45.4	100	65.4	0	0
10546	20.3	40.3	100	74.2	0	0
10547	15.7	35.0	100	97.4	0	0
Mean	19.8	40.8	100	84.6		
Std Dev	2.38	2.96	-	12.2		
RSD (%)	12.0	7.25	-	14.4		

All daily system checks.

TABLE 6 (Continued)

Summary of BFB Validation Tests
Obtained with the HP-5993B after DAC Replacement

	RESOLUTION CRITERIA				
FILE	96/95 .05-.09	173/174 < .02	175/174 .05-.09	177/176 .05-.09	176/174 .95-.101
20004	.065	.019	.0695	.0628	.989
20008	.066	.016	.0750	.0710	.982
10496	.062	.013	.0812	.0666	1.002
10503	.080	.015	.0832	.0801	1.000
10520	.059	.000	.0844	.0786	.993
10526	.065	.000	.0841	.0577	1.007
10546	.070	.000	.0782	.0703	.997
10547	.078	.000	.0821	.0539	1.009
Mean	.0681	.00788	.0797	.0676	.997
Std Dev	.00743	.00857	.00521	.00930	.00912
RSD (%)	10.9	108.8	6.54	13.8	0.914

TEST 2 - SYSTEM STABILITY

This test evaluates the stability of the GC/MS systems as a function of time. The "Test Procedures" specify a 24-hour time period between replicate injections of 50 ng of DFTPP. Acceptable performance is indicated if the spectrum validation test is passed after 24 hours while maintaining identical tuning parameters.

The test was performed twice using DFTPP with a 20-hour and a 64-hour delay. No tuning parameters were changed between the beginning and end of the time period. Overnight, the disc drive was powered down and the computer was halted. The results of the spectrum validation tests for the 20-hour stability study are given at files 10014 and 10016 in Table 3. Both spectra meet all the performance requirements. The spectrum validation tests for the 64-hour stability are given at files 10030 and 10034 on Table 3. Again, both spectra meet all the performance requirements for spectrum validation.

The entries at files 10503 and 10520 in Table 6 represent a 40-hour System Stability Test using 50 ng of BFB for spectrum validation. Sixteen half-hour runs were obtained between validation tests. No retuning was done. Both spectra achieve valid spectrum validation for BFB.

Therefore, the moderate term stability of the HP-5993B is very good and qualifies for routine use.

TEST 3- INSTRUMENT DETECTION LIMIT

This test determines that quantity of DFTPP which can be injected into the system and given an acceptable spectrum validation test, yet remain below a predetermined level of contamination due to ions not present above 3% in the mass spectrum of DFTPP. The test is based on a ratio R such that R is equal to the sum of the relative abundance of the DFTPP ions at m/e 127, 255, 275, 441, 442, and 443, (Σ DFTPP), divided by the sum of the relative abundance of the six most intense non-DFTPP contaminant ions (Σ background). The instrument detection limit is that amount of DFTPP injected which gives R=5.

Sequentially, 50, 40, 30, 20, 10, 5, 1, and 0.1 ng of DFTPP were injected into the HP-5993B. The mass spectrometer was tuned the previous day using AUTOTUNE (Figure 2) and no OVERRIDE corrections were necessary. Figure 2 shows an OVERRIDE report summarizing the current tuning parameters established by AUTOTUNE and the current spectrometer performance with respect to perfluorotributylamine. As mentioned earlier, this test was performed before replacement of the DAC. The value of Mass Axis Gain would now be considered out of tolerance and needs adjustment. The detection limit data were acquired using an electron multiplier setting of 1800 volts, at 5.0 seconds per scan (A/D rate of 8) and a threshold of 1. Electron multiplier performance was documented using the J option in the diagnostic package and is given in Table 7. The detector voltage selected (1800 volts) was the last voltage in Table 7 that produced less than 10000 counts for ion 502.

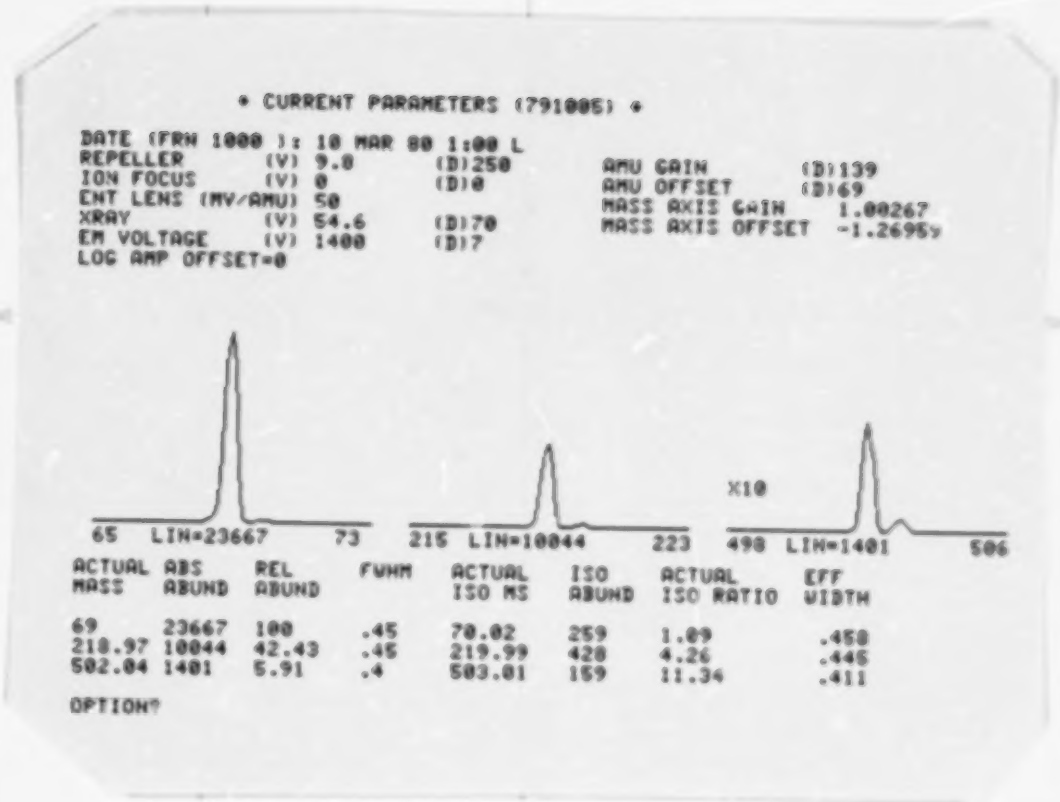
* CURRENT PARAMETERS (791005) *
DATE (FRM 1000): 10 MAR 80 1:00 L
REPELLER (V) 9.0 (D)250
ION FOCUS (V) 0 (D)0
ENT LENS (MV/AMU) 50
XRAY (V) 54.6 (D)70
EM VOLTAGE (V) 1400 (D)7
LOG AMP OFFSET=0
AMU GAIN (D)139
AMU OFFSET (D)69
MASS AXIS GAIN 1.00267
MASS AXIS OFFSET -1.26959
X10
65 LIN=23667 73
215 LIN=10044 223
498 LIN=1401 506
ACTUAL MASS ABS ABUND REL ABUND FWHM ACTUAL ISO MS ISO ABUND ACTUAL ISO RATIO EFF WIDTH
69 23667 100 .45 70.02 259 1.09 .458
218.97 10044 42.43 .45 219.99 428 4.26 .446
502.04 1401 5.91 .4 503.01 159 11.34 .411
OPTION?

Figure 2. OVERRIDE report of mass spectrometer tuning parameters, test 3

TABLE 7

Electron Multiplier Performance During Test 3.

TEST DATE: 11 MAR 80 1:05

DETECTOR		ADC OUTPUT			STEP-BY-STEP GAIN		
STEP	HV	69	219	502	69	219	502
0	0	2	1	1			
1	200	1	1	1	.5	1	1
2	400	1	1	1	1	1	1
3	600	2	1	1	2	1	1
4	800	19	10	2	9.5	10	2
5	1000	400	257	19	21.0526	25.7	9.5
6	1200	3108	2020	158	7.77	7.85992	8.31579
7	1400	14307	9357	828	4.60328	4.63218	5.24051
8	1600	14307	18130	2003	1	1.93759	2.41908
9	1800	14307	18130	5717	1	1	2.85422
10	2000	14307	18130	13376	1	1	2.33969
11	2200	14307	18130	13376	1	1	1
12	2400	14307	18130	13376	1	1	1
13	2600	14307	18130	13376	1	1	1
14	2800	14307	18130	13376	1	1	1
15	3000	14307	18130	13376	1	1	1

Acceptable spectrum validation was achieved at 50, 40, 30, 20, and 10 ng per injection. At 5 ng per injection the relative abundance of mass 127 is 1.8% below the acceptable range and is the only ion not meeting the spectrum validation test. As such, the instrument detection limit must be larger than 5 ng per injection. No R values were calculated for 1.0 and 0.1 ng per injection. At 1 ng DFTPP per injection, only the ratio 443/442 meets the spectrum validation test requirements and ions at m/e 275 and 365 are missing. At 0.1 ng DFTPP per injection, no ion meets the spectrum validation requirements; in fact, the only spectrum validation ions present are at masses 70, 127, 198, 442, and 443.

Table 8 summarizes the results of the Detection Limit Test. The relative abundance of ion 255 is included with the relative abundance of the spectrum validation ions. The mass and relative abundance of the six most intense non-DFTPP ions greater than 3% are also included in Table 7. Since there are fewer than six contaminant ions over 3% relative abundance at 50 and 40 ng per injection, 3% is assigned. The minimum value for (Σ background) is thus 18 and would occur if there were no contaminant ions greater than 3%. The maximum value for Σ DFTPP is 333, assuming ion 255 was at 99% relative abundance. Therefore, the maximum value of R is 333 divided by 18 and is 18.5.

Figure 3 gives a plot of R versus ng per injection. A least squares line was fitted to the results for 50, 40, 30, 20, 10, and 5 ng per injection. That value of nanograms per injection which gives an R value of 5 was calculated to be 25 ng.

Thus the instrument detection limit for the HP-5993B meets the required detection limit (50 ng of DFTPP) for systems to be used for the analysis of industrial or municipal wastes and the required detection limit (30 ng of DFTPP) for systems used for the analysis of ambient or drinking water.

TABLE 8

Results for the Detection Limit Test

Spectrum Validation Ions	Relative Abundance in Percent 50 ng	40 ng	30 ng	20 ng	10 ng	5 ng	1 ng	0.1 ng
51	36.5	34.8	34.9	34.1	39.2	38.2	4.9	0
68	0.2	0.0	0.7	0.0	0.0	0.0	0	0
69	42.4	44.9	39.8	33.0	32.3	17.6	0	28
70	0.7	0.0	0.0	0.0	0.0	0.0	0	2
X 127	46.0	40.9	44.7	45.4	41.5	38.2	9.8	8
197	0.5	0.0	0.3	0.0	0.0	0.0	0	0
198	100.0	100.0	100.0	100.0	100.0	100.0	14.6	2
199	5.5	5.9	5.3	5.9	6.2	8.8	2.4	0
X 275	22.5	21.2	22.0	19.5	10.8	17.6	0	0
365	1.6	1.6	2.0	1.6	3.1	2.9	0	0
X 441	10.4	11.1	11.2	11.4	5.4	11.8	2.4	0
X 442	88.4	92.9	91.8	90.8	49.2	100.0	12.2	2.0
X 443	16.7	17.2	16.1	17.3	10.0	20.6	2.4	2.0
X 255	31.5	30.8	38.9	31.3	24.6	20.6	0	0
(Σ DFTPP)	215.5	214.1	214.7	215.7	141.5	208.8		
Contaminant Ions								
	62-3.6	48-6.1	47- 3.6	44-10.3		46-40.0	46-73.5	
	80-3.1	90-4.5	48-10.9	66-11.4		48-30.0	49-55.9	
	114-3.3	104-3.8	49- 8.9	81-11.4		49-18.5	64-70.6	
	-3	111-3.1	63- 4.3	90- 8.1		52-25.4	80-64.7	
	-3	-3	76- 4.9	102- 9.2		64-19.2	88-50.0	
	-3	-3	83- 5.9	114- 8.1		86-32.3	108-52.9	
(Σ Bckg)	19.0	23.5	38.5	58.5		165.4	376.6	
R =	11.34	9.11	5.58	3.69		0.856	0.568	

x - ions used in (Σ DFTPP)

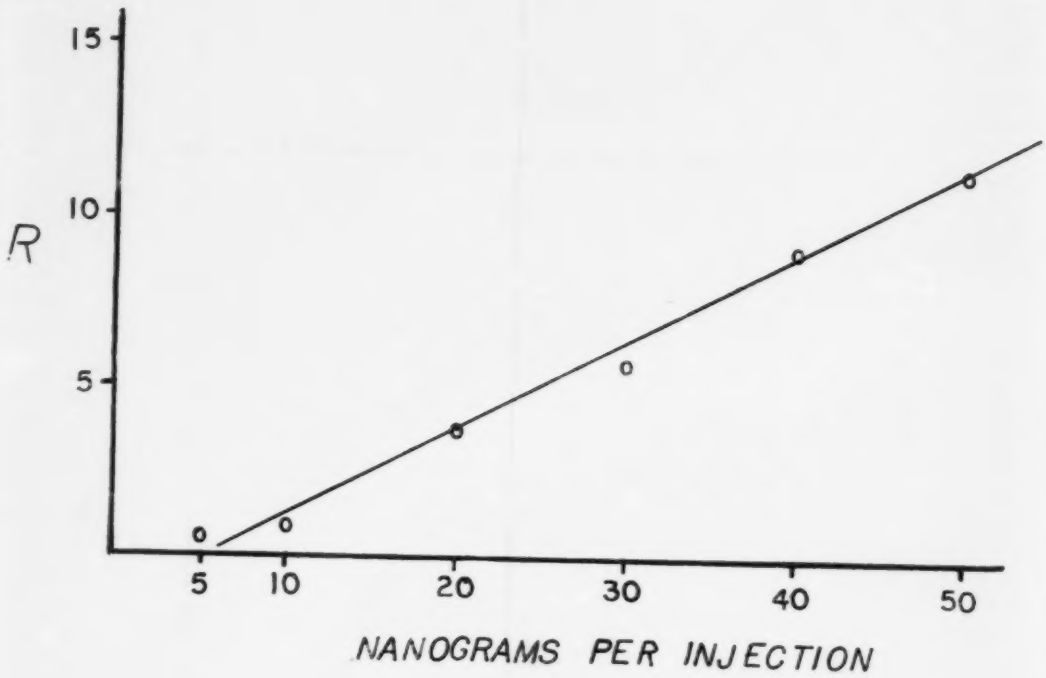

Figure 3. Plot of R versus nanograms per injection, test 3

TEST 4 - SATURATION RECOVERY

This test evaluates the sytems's ability to cope with a situation frequently occurring in the analysis of environmental samples. Specifically, the analyst must obtain the mass spectrum of a relatively small quantity of a particular compound that elutes just after a relatively large quantity of another compound. If the vacuum system doesn't quickly pump off the first compound, or if the background subtracting algorithm is faulty, the mass spectrum of the smaller compound may be contaminated with ions from the first compound. If the detector goes into a saturated state due to a large excess of the first compound and doesn't quickly recover, the system may not acquire a valid spectrum of the second compound.

An acetone solution at 5.51 mg/mL of 4-bromobiphenyl and 22 µg/mL of DFTPP was prepared (250:1). Two microliters of this solution were injected in the HP-5993B giving 11 µg of 4-bromobiphenyl and 44 ng of DFTPP on column.

GC-CONDITIONS: Same column as Test 1, 3% OV-17; Oven 5 minute hold at 150°C then 10° per minute to 250°C; Injector Port, 250°C; Carrier gas, helium at 30 mL per minute.

MS CONDITIONS: Repetitive scans from 40 to 450 amu; 5.0 seconds per scan (A/D=8); and a threshold of 10. Tuning conditions are identical to those in Test 3.

CNORM FILE: Obtained from File 10052, 50 ng of DFTPP run just prior to Test 4.

The retention time of 4-bromobiphenyl was 10.3 minutes (31 scans) and the retention time of DFTPP was 11.5 minutes (48 scans). The total ion current profile from this run is given in Figure 4. Table 9 lists the raw mass spectra for the 11 µg of 4-bromobiphenyl after CNORM, mass and actual abundance are tabulated. The largest ion abundance reported is 12,032 counts at mass 152, the base peak for 4-bromobiphenyl. Since this is less than 32,767 counts, the detector did not saturate. The $^{81}Br/^{79}Br$ ratio at masses 234 and 232 is 0.963 which is quite acceptable.

The background corrected mass spectra of 44 ng DFTPP which eluted 1.3 minutes after 4-bromobiphenyl is given in Table 10 mass and relative abundance are tabulated, and contains no ions at masses 76, 152, 232, or 234, the four most intense ions in 4-bromobiphenyl. The mass spectrum of DFTPP meets the criteria of the spectrum validation test (File 10054, Table 3). Therefore, the HP-5993B demonstrates excellent saturation recovery.

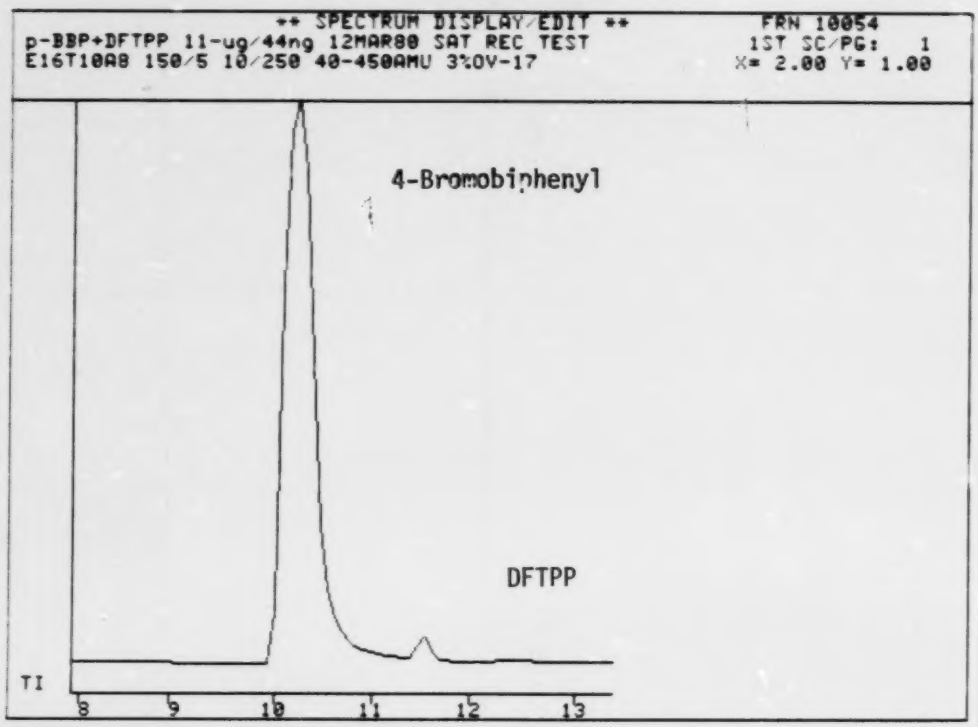

Figure 4. Total ion current profile for 4-Bromobiphenyl and DFTPP, test 4.

TABLE 9

Mass Spectrum of 11 Micrograms of 4-Bromobiphenyl, Test 4.

FRN 10054 SPECTRUM 30 RET. TIME = 10.3
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40.1	157.	69.0	51.	95.0	33.	121.0	51.
		70.1	9.	96.0	11.	122.0	179.
41.1	59.	71.1	16.	97.1	114.	123.0	107.
42.1	14.	73.0	373.	98.0	959.	124.1	79.
43.1	104.	74.1	2895.	99.1	670.	125.1	443.
44.1	21.	75.0	3796.	100.1	303.	126.0	2203.
45.1	10.			101.1	895.	127.1	1574.
		76.1	7593.	102.1	1100.	128.1	235.
49.1	285.	77.1	2069.	103.1	223.	129.0	32.
50.1	4051.	78.1	290.			129.9	43.
51.1	3796.	78.9	203.	103.9	134.	131.0	23.
52.1	724.	80.0	74.	104.9	38.		
53.0	104.	81.0	166.	105.9	59.	132.0	11.
55.1	48.	82.0	72.	106.9	31.	134.1	11.
56.0	29.	83.0	16.	108.2	18.	135.1	9.
57.0	35.	84.0	40.	109.1	100.	137.1	48.
58.1	20.	85.0	336.	110.0	230.	138.1	54.
60.1	37.	86.0	903.	111.0	279.	139.0	44.
61.1	568.	87.0	1184.	112.1	77.	140.0	10.
		88.0	514.	113.1	491.	141.0	19.
62.1	1604.	89.0	417.	114.1	475.	141.9	9.
63.0	4347.			115.1	343.	142.9	26.
64.0	337.	90.1	102.	116.0	853.	144.1	8.
65.0	172.	91.0	66.	117.0	938.	145.0	16.
66.0	19.	92.0	12.				
67.1	15.	93.0	41.	119.0	76.	146.0	20.
68.3	13.	94.0	10.	120.0	29.	147.0	18.

FRN 10054 SPECTRUM 30 RET. TIME = 10.3

MASS	ABUND	MASS	ABUND
149.1	148.	217.0	5.
150.1	1345.	218.9	5.
151.1	3236.	221.1	4.
152.1	12032.	226.0	4.
153.1	3397.	226.9	5.
154.2	385.		
155.0	46.	232.0	5729.
156.0	15.	233.0	886.
157.0	12.	234.0	5516.
157.9	9.	235.0	741.
		236.0	48.
165.0	9.		
167.0	9.	259.1	6.
169.1	9.		
		355.1	2.
180.0	27.	>PAUSE	
181.0	7.		
182.0	30.		
193.0	26.		
194.0	6.		
195.0	25.		
204.0	9.		
205.9	25.		
207.0	7.		
208.0	17.		

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TABLE 10

Mass Spectrum of 44 ng DFTPP, Test 4

WORK AREA FRN 10054 + 47 -45
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40	1.7	77	44.1	118	2.3	163	.2
41	.6	78	2.3	120	.6	165	.2
47	.4	79	1.7	122	2.9	166	.5
		80	1.7	127	48.7	167	2.9
48	2.3	81	3.4	128	3.2	168	2.9
49	2.1	82	.8	129	20.0	169	.2
50	8.4	85	.4	130	1.5		
51	37.0	86	.2			175	1.9
52	2.3			133	.2	177	.6
55	.2	91	.6	135	.8	178	.2
56	.8	92	.2	136	.2	179	1.7
57	1.3	93	3.8	137	.2	180	.6
58	1.5	96	2.1	140	1.9	181	.6
59	.2	98	1.9	141	1.0	182	.4
61	2.1	99	3.6	142	2.3	185	1.9
		101	1.7	143	2.1	186	8.2
63	.4			145	.2	187	2.9
63	2.3	104	1.0				
65	.8	105	.4	146	1.7	191	.2
67	.8	106	.6	148	1.3	192	1.0
68	.8	107	13.4	156	1.3	193	.8
69	53.8	108	1.7	157	.4	194	1.0
70	.2	110	35.1	158	1.7	195	.4
72	2.5	111	4.4	159	.4	196	1.9
74	3.2	116	.2			197	.8
75	7.4	117	7.4	160	1.5	198	100.0
				161	.6	199	[illegible]

WORK AREA FRN 10054 + 47 -45

MASS	ABUND	MASS	ABUND	MASS	ABUND
200	1.0	257	.2	372	.8
204	1.9	258	1.9	394	.4
205	2.5	261	.2		
206	14.1	265	.4	402	.4
207	2.3			403	.6
208	.2	273	1.0		
209	.4	274	3.6	421	.2
211	.8	275	18.7	422	.4
		276	3.4	423	3.2
217	3.6	277	1.5	424	.6
218	1.3				
221	3.6	296	3.4	441	6.3
223	.8	297	.6	442	53.8
224	7.6			443	9.7
225	2.5	303	.6	444	.8
227	2.9			>PAUSE	
228	.8	315	.4		
229	1.0	316	.4		
		323	1.5		
244	6.5				
245	1.3	328	.6		
246	1.0	332	.4		
253	.2	334	1.0		
254	1.0				
255	26.7	365	1.3		
256	4.4				

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TEST 5 - PRECISION TEST

This test measures the precision for replicate quantitative analysis by direct injection using continuous repetitive measurement of spectra. Sources of variability range from the variation inherent in refilling a microsyringe, to aging of the detector, to variations encountered when integrating the peak area of a specific quantitation ion. This test was performed using semivolatile compounds and compounds amenable to purge and trap analysis.

A solution of 20 µg/mL each of 1,2,4-trichlorobenzene, hexadecane, dimethylphthalate, hexachlorobenzene, aldrin, dibutylphthalate, and pyrene was used for this test. The "Performance Test" requires at least seven compounds: one must be a chlorinated hydrocarbon that could decompose on a hot metallic surface and one must be a polycyclic aromatic hydrocarbon of molecular weight greater than 200. Eight sequential analyses of a 4 µL aliquot of the standard solution were performed. A ten microliter syringe equipped with a Chaney adaptor was used. Each injection contained 80 ng of each compound.

GC CONDITIONS: Column, 1.8 m x 2 mm ID glass column packed with 1% SP-2250; Oven, 10°C for 3 minutes than 10° per minute to 280°C; Injector Port, 270°C; and carrier gas, helium at 30 mL per minute.

MS CONDITIONS: Repetitive scans from 30 to 400 amu; 4.0 seconds per scan (A/D=7); and a threshold of 10. Tuning conditions were AUTOTUNE conditions with AMU OFFSET raised one unit.

CNORM FILE: Based on an injection of 50 ng of DFTPP (file 10112, Table 3) obtained immediately prior to the start of Test 5. The spectra were collected without CNORM correction so that precision before and after the application of CNORM could be studied.

Figure 5 shows the total ion current profile obtained during the fourth replicate injection. The trichlorobenzene (A) and dimethylphthalate (C) peaks exhibit rather severe tailing, the other compounds give sharp, well defined peaks. After all eight replicates were obtained, various integration routines were used to measure the peak areas of the quantitation masses both before and after correction by the CNORM file. Table 11 summarizes the precision statistics both before and after application of CNORM utilizing manual integration. The mean of the relative standard deviations (RSDs) before application of CNORM was 3.25% (3.45% pooled) and 3.43% (3.74%) after application of CNORM. The pooled RSD, which is the square root of the mean of the sum of the squares of the individual RSDs, is reported because the pooled RSD is a better measure of the total variance compared to the mean value of the individual RSDs. The mean area for each quantitation mass greater than m/e 140 dropped by more than 50% after CNORM was used; however, the pooled RSD only changed from 3.45 to 3.74%. It is clear that the application of the CNORM file reduces raw abundances, but hardly affects the precision for integration. Since the CNORM adjustment is done using division by numbers larger than 1 and less than 8, no ion abundance larger than the individual divisor disappear after CNORM adjustment.

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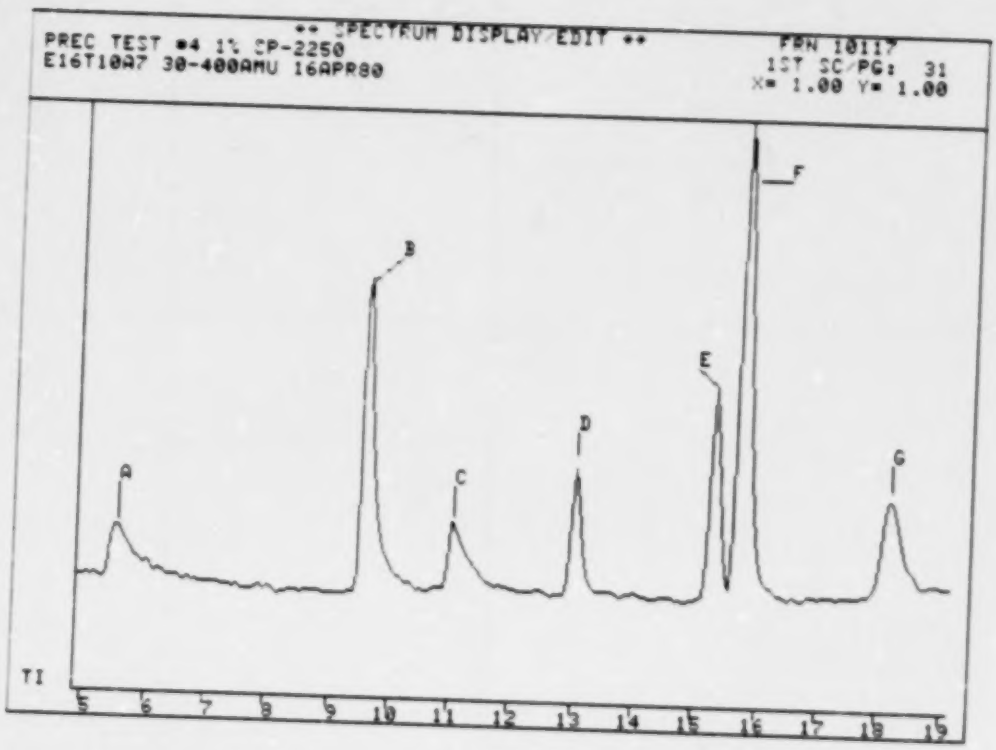

Figure 5. Total ion current profile for test 5.

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TABLE 11

Precision Statistics Obtained Using Manual Integration
Before and After Application of CNORM

Compound	Integration Mass	Mean Area (n = 8)	Standard Deviation	RSD in Percent
Before CNORM				
A 1,2,4-trichlorobenzene	180	4355	190	4.36
B Hexadecane	57	7849	337	4.29
C Dimethylphthalate	163	11328	259	2.29
D Hexachlorobenzene	284	2737	53.0	1.94
E Aldrin	66	2361	45.7	1.94
F Dibutylphthalate	149	51012	1517	2.97
G Pyrene	202	12293	609	4.95
			Mean	3.25
			Pooled Mean	3.45
After CNORM				
A 1,2,4-trichlorobenzene	180	1973	112	5.68
B Hexadecane	57	7864	363	4.62
C Dimethylphthalate	163	5074	105	2.07
D Hexachlorobenzene	284	1291	24.1	1.87
E Aldrin	66	1910	36.4	1.91
F Dibutylphthalate	149	23646	668	2.83
G Pyrene	202	4916	246	5.00
			Mean	3.43
			Pooled Mean	3.74

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Table 12 summarizes the precision statistics for external and internal standard quantitation, after CNORM, using the automated integration program QUANTID. The mean of the RSDs is 4.26% (4.53% pooled). It is interesting to note that compound A, which exhibits tailing, gave the largest RSD when automated integration was used but not when manual integration was used.

Both the mean RSD and pooled RSD for external standard quantitation using automated integration fall within the 7% requirement as given in the "Performance Tests." The pooled RSD for external standard quantitation using peak height measurements was 7.33%. As such, external standard quantitation based on peak height measurements using a scan rate of 4.0 seconds is unacceptable for routine analysis.

The precision statistics for response factors as reported by QUANTID using dibutylphthalate as an internal standard are also reported in Table 12. Internal standard quantitation calculations compensate for the variability inherent in refilling a microsyringe and for aging of the detector and are more indicative of the precision of the HP-5993B system. The mean RSD for the response factors is 3.06% (3.23% pooled) and is well within the 7% requirement stated in the "Performance Tests."

Another precision test was performed using the volatile organic compounds used in Test 8. The results for Test 8 depend heavily upon the reproducibility between syringe injections into a hot injector port compared to syringe injections into a cold 5.0 mL aliquot of reagent water. Good purge and trap techniques demand adding no more than 1 µL of methanol to the 5.0 mL sample contained in the purging vessel. If more than 1 µL of methanol is present, the bubble size of the purging gas changes and erratic purging efficiencies can be obtained. Since publication of the "Performance Tests," a 1.0 µL zero dead volume syringe has been recommended to manipulate the 1.0 µL aliquots of methanolic standards used in Test 8. However, one is never sure that the zero dead volume syringe is filled. To overcome these problems, a standard 10-µL syringe was used to dispense 3-µL aliquots of a 30% methanol, 70% water (V:V) solution of standards to give good reproducibility for refilling the syringe yet stay below the 1 µL methanol per 5.0 mL sample restriction.

Table 13 summarizes the precision study for six direct injections of 3.0 µL aliquots of a 30% methanol, 70% water solution of volatile organics injected into a 150°C injector port. All peaks were sharp and well defined (Figure 7, Test 8). For external standard quantitation, the mean RSD was 3.30% (3.61% pooled). For internal standard quantitation using benzene as the internal standard, the mean RSD for the response factor measurements was 2.91% (3.12% pooled).

Overall, the HP-5993B gave excellent results for Test 5. Use of peak height measurements for external standard quantitation gave a pooled RSD of 7.33% and is unacceptable for routine analyses. The "Performance Tests" require a mean RSD of less than 7%. The HP-5993B gave excellent precision for both external standard (4.53 and 3.61%) and internal standard quantitation (3.23 and 3.12%) using automated area measurements. As such, the HP-5993B easily meets the precision test requirements described in the "Performance Tests."

TABLE 12

Precision Statistics Obtained Using Automated Integration
After Application of CNORM

Compound	Integration Mass	Mean Area (n = 8)	Standard Deviation	RSD in Percent
Using External Standards				
A 1,2,4-trichlorobenzene	180	1519	106	6.98
B Hexadecane	57	7200	288	4.00
C Dimethylphthalate	163	4151	191	4.60
D Hexachlorobenzene	284	1308	22.5	1.72
E Aldrin	66	2193	90.0	4.10
F Dibutylphthalate	149	23568	710	3.01
G Pyrene	202	4807	260	5.42
			Mean	4.26
			Pooled Mean	4.53
Using Dibutyl Phthalate as the Internal Standard		Mean Response Factor		
A 1,2,4-trichlorobenzene	180	0.064	0.0032	5.00
B Hexadecane	57	0.305	0.0054	1.77
C Dimethylphthalate	163	0.176	0.0050	2.84
D Hexachlorobenzene	284	0.055	0.0012	2.18
E Aldrin	66	0.093	0.0029	3.12
F Dibutylphthalate	149	1.000	0.0000	-
G Pyrene	202	0.203	0.007	3.45
			Mean	3.06
			Pooled Mean	3.23

Integration Threshold = 25
Threshold for Standard = 150
Retention Time Scan Window = 20
Threshold for Compounds = 150

Table 13

Precision Statistics For Volatile Organics
Direct Septum Injections

Compound	Integration Mass	Mean Area (n = 6)	Standard Deviation		RSD in Percent
External Standards					
A Chloroform	83	2275	134		5.89
B Carbon tetrachloride	117	1525	76.6		5.02
C Bromodichloromethane	83	2118	38.7		1.83
D Trichloroethene	130	1782	90.6		5.08
E Benzene	78	4105	107		2.61
D Bromoform	173	1568	46.2		2.95
G 1,1,2,2-Tetrachloroethane	83	2633	57.5		2.18
H Toluene	91	4592	177		3.85
I Chlorobenzene	112	3550	81.5		2.30
J Ethylbenzene	91	6158	162		2.63
K 4-Bromofluorobenzene	174	2507	66.2		2.64
				Mean	3.36
			Pooled Mean		3.61
Using Benzene as an Internal Standard		Mean Response Factor n = 6			
A Chloroform	83	0.558	0.0184		3.30
B Carbon tetrachloride	117	0.375	0.0176		4.69
C Bromodichloromethane	83	0.520	0.0111		2.13
D Trichloroethene	130	0.437	0.0159		3.64
E Benzene	78	1.000	0.000		--
D Bromoform	173	0.385	0.0120		3.12
G 1,1,2,2-Tetrachloroethane	83	0.646	0.0272		4.21
H Toluene	91	1.128	0.0386		3.42
I Chlorobenzene	112	0.876	0.0119		1.36
J Ethylbenzene	91	1.511	0.0161		1.07
K 4-Bromofluorobenzene	174	0.615	0.0132		2.15
				Mean	2.91
			Pooled Mean		3.12

Integration Threshold = 25
Threshold for Standard = 150
Retention Time Scan Window = 17
Threshold for Compounds = 150

TEST 6 - LIBRARY SEARCH TEST

A 14 AMU library search and a Probability Based Search (PBS) library search are available as distinct options with the HP-59938. The 14 AMU search is the older of the two options and its compatible NBS library, molecular weights 1 to 1674, containing more than 15,000 entries, occupies two 7900 discs. The PBS software is newer and its compatible NBS library, molecular weights 1 to 9999, greater than 28,000 entries, occupies six 7900 discs. Any PBS library mass spectrum can be plotted. With 14 AMU software, no library spectra can be plotted, only header information is available.

Figure 6 shows the total ion current profile for the GC/MS data file used for the library search test. The data file was corrected using a CNORM file generated at the beginning of the day. The average time needed to obtain a background corrected mass spectra was 55 seconds when done manually and 6 seconds when done using the BATCH PK, LS command. Library searching averaged 53 seconds per search using the 14 AMU software and library, and averaged 118 seconds per search using the PBS software and library. Manual background subtracting averages about 5 seconds using revision D software. In either case, the identical spectra were searched, the only difference was the search software and library. The mass range of 30 to 400 amu was specified for each search.

The results for the 14 AMU software library search are summarized in Table 14. The hard copy output included the name, library number, molecular weight, and molecular formula of each compound that was assigned a "hit." No Chemical Abstracts Service registry (CAS) numbers were reported. The 14 AMU library search was successful for the five compounds ranked number one and for 1,2,4-trichlorobenzene. Dibutylphthalate was ranked second behind tert-butyl hydrazine oxalate when the spectrum obtained using BATCH was searched against disc 2 of the library; however, this ranking reversed when the manually subtracted spectrum was searched. Considering that the dibutyl phthalate peak (G) is fused on the tail of the aldrin peak (F) in the total ion current profile and that the background subtracted spectra obtained manually in this complex region of the chromatogram gave dibutyl phthalate ranked number one, this search can be considered successful. The search for benzo(a)pyrene (I) gave no hit. The NBS library spectrum for benzo(a)pyrene - (EPA/NIH Mass Spectral Data Base, vol. 2, p. 1780, December 1978) shows P-2 at less than 2% when in fact P-2 is about 15%. Because of this error in the data base, a library search giving no hit for benzo(a)pyrene cannot be considered unsuccessful.

The results for the PBS software library search are summarized in Table 15. The hard copy output included the probability of the match, a molecular ion indicator, the name, the library number, the molecular weight, the molecular formula, the NBS number, the CAS number and an EPA number of the match. Other output identified the percent of missing and contamination peaks, the number of peaks in the unknown spectra, and the number of peaks in the unknown that matched peaks in the reference spectrum. The PBS library search was considered successful for all nine compounds. Seven compounds were ranked first and 1,2,4-trichlorobenzene was again ranked third behind 1,2,3- and 1,3,5-trichlorobenzene. Hexadecane was ranked

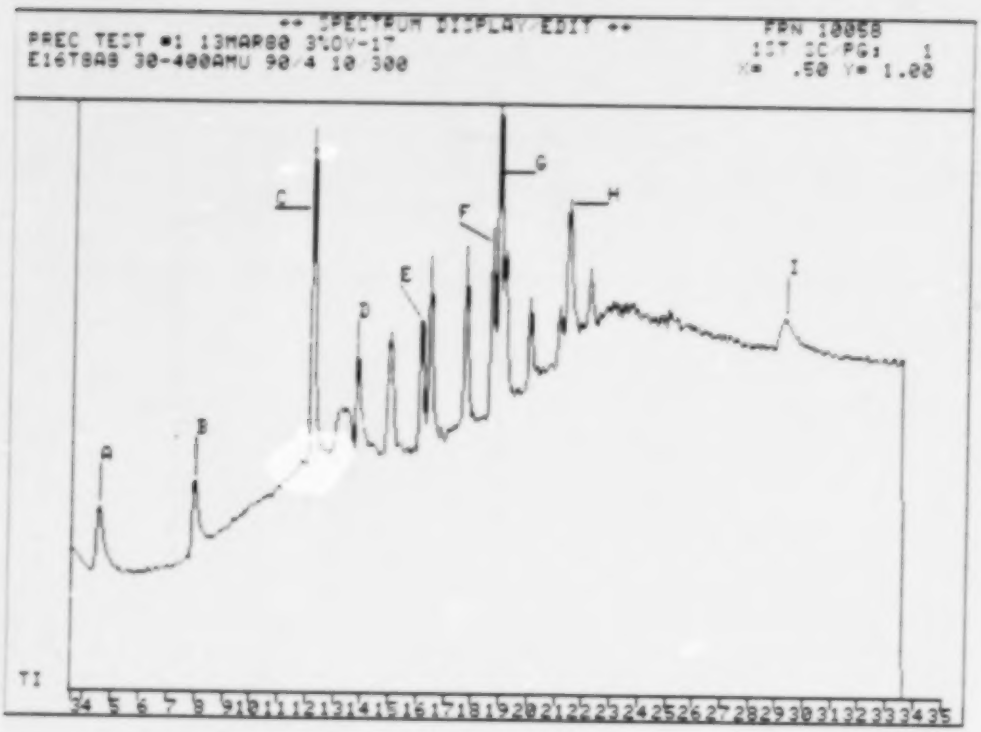

Figure 6. Total ion current profile of data used for library search test

TABLE 14

Results of the Library Search Test
Using 14 AMU Software

Compound (mol weight)	Disc 1 1 to 350 amu.	Disc 2 165-1674 amu.	Command Ranked Highest
A 1,2-Dichlorobenzene (146)	2	*	Methyl 1-(4-chlorophenyl)-3-thioxo-4-thia-1 hydroxy heptenoate.
B 1,2,4-Trichlorobenzene(180)	3	3	1,2,3-Trichlorobenzene on both discs.
C Hexadecane (226)	1	1	
D Dimethylphthalate (194)	1	1	
E Hexachlorobenzene (282)	1	1	
F Aldrin (362)	*	1	
G Dibutylphthalate (278)	5	2**	Disc 1: tert-butyl hydrazine hydrochloride Disc 2: tert-butyl hydrazine oxalate.
H Pyrene (202)	1	1	
I Benzo(a)pyrene (252)	No hit	No hit	
Mean Search Time	52 sec	54 sec	

* Spectrum not present on library disc.
** Ranked 1 when manually corrected spectra was searched.

TABLE 15

Results of the Library Search Test Using PBS Software

Compound	Rank	Compounds Ranked Higher
A 1,2-Dichlorobenzene	1	
B 1,2,4-Trichlorobenzene	3	1,2,3- and 1,3,5-trichlorobenzene
C Hexadecane	3	Octacosane, Pentacosane
D Dimethylphthalate	1	
E Hexachlorobenzene	1	
F Aldrin	1	
G Dibutylphthalate	1	
H Pyrene	1	
I Benzo(a)pyrene	4	Three isomers of benzo(a)pyrene
Mean Search Time	118 sec	

third, behind octacosane and pentacosane. The hardcopy output indicated that the molecular ion for hexadecane was present at the correct abundance for hexadecane but not for octacosane nor pentacosane. Benzo(a)pyrene was ranked fourth behind three isomeric polycyclic aromatic hydrocarbons.

The "Performance Tests" require a 100% success rate when background corrected mass spectra are searched against the EPA/NIH data base or a subset thereof containing at least 10,000 entries and that the mean search time be one minute or less. The search time includes both the time used for background correction and the time for the actual search. The HP-5993B equipped with 14 AMU search software meets all of the requirements. For the HP-5993B equipped with PBS search software, all but one of the requirements are met: the mean search time, 118 seconds when automated background corrections are made, is almost double the maximum search time of one minute. The 14 AMU software would be preferred because of the speed of the search. The PBS software would be preferred because of the ability to plot library spectra. Under ANSWER software, the library spectra for the top hit is automatically output to the CRT and the difference between this library spectrum the top five hits is also presented on the CRT.

TEST 8 - QUANTITATIVE ANALYSIS WITH INERT GAS PURGE AND TRAP

This test measures the accuracy and precision of the GC/MS system for inert gas purge and trap analyses of volatile organic compounds. Since reagent water is used for the sample matrix, the results obtained should be optimal because the results aren't complicated by real sample matrix effects. An integral part of the test is the measurement of the purging efficiency which is characteristic of the purge and trap equipment interfaced to the GC/MS.

A standard solution of eleven volatile organic compounds (Table 15) each at 33 ng per µL in 30% methanol, 70% water (V:V) was used for this test. The "Performance Tests: require that chloroform, bromoform, 1,1,2,2-tetrachloroethane and 4-bromofluorobenzene (BFB) be included in the test mix. The solvent flush technique using a 1.0 µL plug of water and a 1 µL plug of air was used to inject a 3.0 µL aliquot of the standard solution into either the hot injection port or into each 5.0 mL sample of reagent water. Again, a ten microliter syringe equipped with a Chaney adaptor was used.

Determination of the purging efficiency demands the comparison of the response obtained after direct septum injections to the response obtained from purge and trap runs. The HP-7675A purge and trap unit is interfaced to the GC column using a syringe needle that is screwed into the septum retainer nut and has a carrier gas flow controller that is independent of the GC flow controller. As such, it is impossible to make direct injections when the purge and trap unit is interfaced to the HP-5993B. The unit can be switched over from the purge and trap mode to direct injection mode during the five minutes that the oven is cooling between runs. To make the switch over requires removing the HP-7675A syringe needle and septum retaining nut, replacing the septum nut with the standard septum nut, and increasing the carrier gas flow at the GC flow controller to give 0.8 Torr on the jet separator vacuum gauge. To go back to the purge and trap mode requires switching the septum retainer nuts, inserting and screwing down the syringe needle and decreasing the GC carrier flow to give 0.8 Torr on the vacuum gauge.

Of the nine runs made for Test 8 (Files 10146 to 10154, Table 5) runs 1, 5, and 9 were direct injections and runs 2, 3, 4, 6, 7 and 8 were purge and trap runs. The purge and trap samples were prepurged for 1.0 minute, purged for 11.0 minutes at 40 mL per minute, and desorbed at 180°C for 4.0 minutes. The purging vessel was identical for all runs and the standard Tenax-GC trap was used. The retention time clock was zeroed at the start of the prepurge cycle for purge and trap runs, and zeroed at the moment of injection for direct injection runs. During the prepurge cycle, cool air is blown over the heat sink of the trap for a specified time to ensure that the trap is at room temperature.

GC CONDITIONS: Column: 1.8 m x 2 mm ID glass column packed with 1% SP-1000 on Carbopak B; Oven: purge and trap - 45°C for 15 minutes then 10° per minute to 225°C, direct injection - 45°C for 3 minutes then 10° per minute to 225°C; Injector Port, 150°C; and Carrier gas, helium at 30 mL per min.

MS CONDITIONS: Repetitive scans from 20 to 220 amu; 4.0 seconds per scan (A/D=13); and a threshold of 8; Tuning parameters; AUTOTUNE values with AMU OFFSET lowered 1 unit, AMU GAIN raised 1 unit and EM voltage raised 200 volts.

CNORM FILE: Not used for mass range 20 to 220 amu.

A typical total ion current profile for a purge and trap run is given in Figure 7. All peaks are sharp. Even though carbon tetrachloride (B) and bromodichloromethane (C) are not fully resolved on the total ion current profiles, quantitation went smoothly using extracted ion current profiles for each quantitation mass. Table 16 summarizes the purging efficiency study for these eleven volatile organic compounds. Purging efficiency is the ratio of the mean area by purge and trap to the mean area by direct injection times 100%. The mean of all eleven purging efficiencies is 87% with a range of 58 to 96%. The "Performance Tests" require that the mean be greater than 70% with no individual value less than 30%. The required average purging efficiency for chloroform (> 90%) has been changed to greater than 30%.

The area of each compound in the third purge and trap run was used to calculate the precision for external standard quantitation during purge and trap analyses. Table 17 summarizes the results. Only five replicates are used in Table 17, because the third purge and trap run is now considered a calibration run.

The mean of the P values (P) is 100.3% and the mean RSD of the P values is 6.54% (7.02% pooled). The "Performance Tests" require that P be within the range 90 to 110% and that the mean RSD be less than 19%.

The third purge and trap run was also used to generate response factors for each compound relative to benzene to determine the precision of internal standard quantitation during purge and trap analyses. Table 17 also summarizes these results. Benzene was selected as the internal standard because it elutes in the middle of the total ion current profile. The mean P value (P) is 100.4% and the mean RSD of the P values is 3.90% (4.18% pooled).

The HP-7675A and HP-5993B cominbation for purge and trap analyses by GC/MS easily meets all the requirements stated on the "Performance Tests" for the eleven compounds studied. The HP-5993B also meets the spectrum validation criteria for BFB using either purge and trap or direct septum injections.

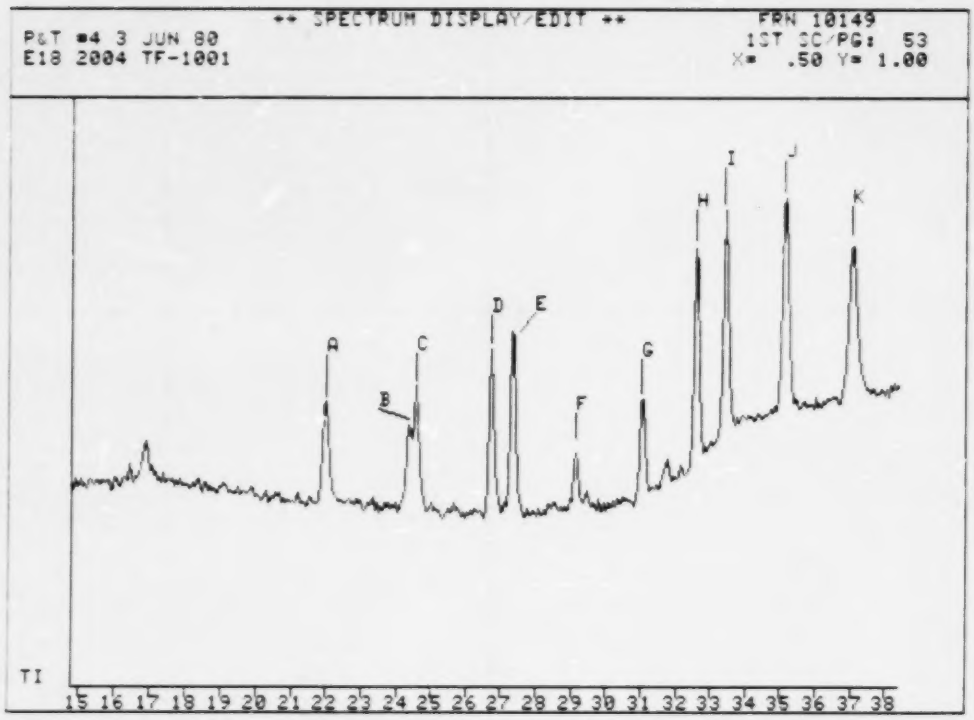

Figure 7. Total ion current profile for eleven compounds by purge and trap, test 8.

TABLE 16

Purging Efficiencies for Eleven
Volatile Organic Compounds - Test 8

Compound	Integration Mass	Mean Area Purge & Trap n = 6	Mean Area Direct Inj. n = 3	Mean Purging Efficiency %
A Chloroform	83	2084	2230	93
B Carbon tetrachloride	117	1166	1310	89
C Bromodichloromethane	83	1932	2013	96
D Trichloroethene	130	1318	1467	88
E Benzene	78	3574	3847	93
F Bromoform	173	724	1133	64
G 1,1,2,2-Tetrachloroethane	83	1416	2460	58
H Toluene	91	3654	3953	92
I Chlorobenzene	112	2964	3100	96
J Ethylbenzene	91	4876	5330	91
K 4-Bromofluorobenzene	174	1748	1880	93
			Mean	87

Integration Threshold = 25
Threshold for Standard = 150
Retention Time Window =17
Threshold for Compounds = 150

TABLE 17

Precision of the HP-7575A - HP-5993B
Purge and Trap Analyses

Compound	Integration Mass	Mean P n = 6	Mean P n = 3	Percent %
A Chloroform	83	100.2	3.77	3.76
B Carbon tetrachloride	117	105.0	12.3	11.7
C Bromodichloromethane	83	96.9	6.83	7.05
D Trichloroethene	130	96.2	10.2	10.6
E Benzene	78	101.4	6.01	5.93
F Bromoform	173	103.5	6.57	6.35
G 1,1,2,2-Tetrachloroethane	83	97.6	4.58	4.69
H Toluene	91	103.5	7.65	6.75
I Chlorobenzene	112	100.3	6.77	6.75
J Ethylbenzene	91	99.4	3.00	3.02
K 4-Bromofluorobenzene	174	99.4	4.66	4.69
		$\bar{P}$ = 100.3	Mean	6.54
			Pooled Mean	7.02
Using Benzene as an Internal Standard				
A Chloroform	83	101.6	5.10	5.02
B Carbon tetrachloride	117	104.0	7.10	6.81
C Bromodichloromethane	83	97.0	2.27	2.34
D Trichloroethene	130	96.8	4.00	4.13
E Benzene	78	-	-	-
F Bromoform	173	103.5	3.44	3.33
G 1,1,2,2-Tetrachloroethane	83	98.4	4.68	4.76
H Toluene	91	104.0	1.33	1.28
I Chlorobenzene	112	98.0	2.95	3.01
J Ethylbenzene	91	100.0	4.94	4.94
K 4-Bromofluorobenzene	174	100.1	3.40	3.40
		$\bar{P}$ = 100.3	Mean	3.90
			Pooled Mean	4.18

Integration Threshold = 25
Threshold for Standard = 150
Retention Time Window =17
Threshold for Compounds = 150

TEST 9 - QUALITATIVE ANALYSIS WITH REAL SAMPLES

This test evaluates both the GC/MS system and the individual laboratory with respect to qualitative analyses of real environmental samples containing natural backgrounds and interferences. An acetone standard containing 140 µg per mL each of acenaphthylene, fluorene, 2-methylanthracene, pyrene, chrysene, benzo(a)pyrene and benzo(ghi)perylene was prepared and analyzed. A 0.75 mL aliquot of the final extract of an NBS sediment sample was analyzed before and after dosing with 0.25 mL of the standard solution.

GC CONDITIONS: Column, 1.8 m x 2 mm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport; Oven, 150°C for 3 minutes than 8° per minute to 280°C; Injector Port, 280°C; Carrier gas, helium at 30 mL per minute.

MS CONDITIONS: Repetitive scans from 30 to 350 amu; 3.9 seconds per scan (A/D=8); and a Threshold of 15; Tuning parameters; AUTOTUNE results with AMU OFFSET increased 2 digital units and EM voltage raised 200 volts.

CNORM FILE: Obtained from 50 ng of DFTPP (File 10063, Table 3) just prior to the run.

Figure 8 displays the total ion current profile for the three GC/MS runs used for this test: run 1 is a 5.0 µL injection of the final extract, run 2 is a 7 µL injection of the dosed extract, and run 3 is a 2.0 µL injection of the standard solution. Background corrected mass spectra were obtained manually using an extracted ion current profile for the parent ion of each compound of interest to locate the apex of each peak. Background subtraction averaged 41, 34, and 20 seconds per compound for runs 1, 2, and 3 respectively, using revision C software.

The results of the library search using PBS software are summarized in Table 18. No results are reported for 2-methylanthracene since the standard had degraded to give peaks C and E (run 3, Figure 8), neither of which gave mass spectra that fully matched the authentic spectra of 2-methylanthracene or 2-methyl-9, 10-anthraquinone. Neither acenaphthylene (A) nor fluorene (B) were present in the undosed extract, but both were successfully identified in the dosed extract. Of the six compounds in the dosed extract that were submitted to library searching, three were ranked first, two were ranked second, and one was ranked fifth. Since acenaphthylene (P=152) was ranked second behind biphenylene (P=152), and benzo(a)pyrene was ranked fifth behind four isomers, these two searches can be considered successful. The library search for the undosed extract gave pyrene (P=202) ranked first ahead of fluoranthene (P=202) and 7H-benz(de)anthracen-7-one (P=230). For the dosed extract, 7H-benz(de)anthracen-7-one was ranked first ahead of pyrene and fluoranthene. Examination of the individual spectra submitted for searching showed that m/e 230 was present in both cases. Extracted ion current profiles for masses 230 and 202 showed that mass 230 maximized two spectrum numbers before mass 202. Below mass 230, these three compounds have virtually identical mass spectra. Therefore, the library search for pyrene can be considered successful. One of the options in PBS software

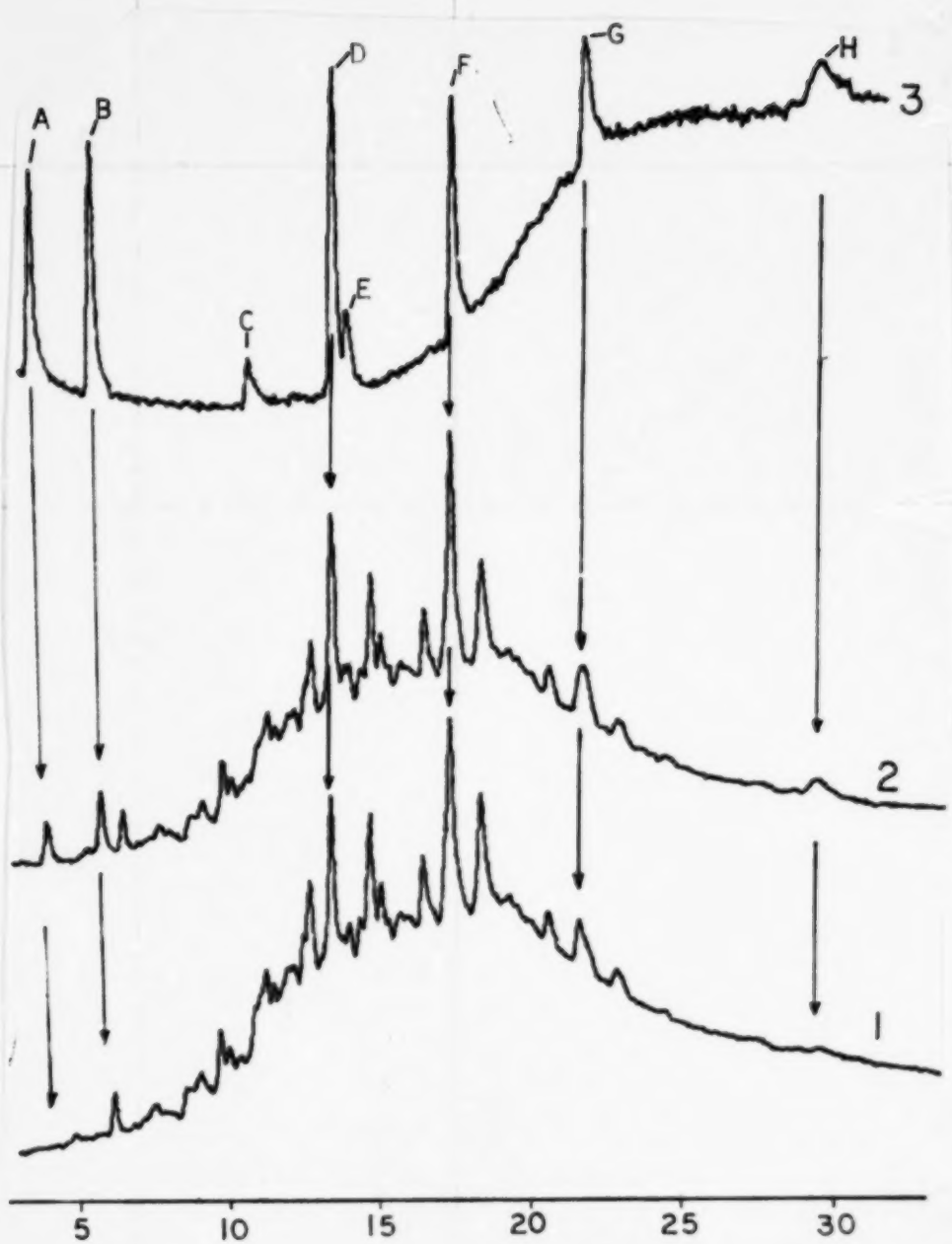

Figure 8. Total ion current profiles for test 9.

permits the user to specify a similarity search or a component search. The similarity search assumes that the unknown is a pure compound and this type of search was used. The component search assumes that the unknown is a mixture, which indeed is the case, and had this type of sarch been used, the results for the pyrene search may have been different.

TABLE 18

Results of PBS Library Search for Test 9

Compounds	Rank In Extract	Rank In Dosed Extract	Compounds Ranked Higher
A Acenaphthylene	Not Present	2	Biphenylene
B Fluorene	Not Present	1	
D Pyrene	1	2	7H-Benz(de)anthracen-7-one
F Chrysene	1	1	
G Benzo(a)pyrene	5	5	All isomers of molecular weight 252
H Benzo(ghi)perylene	1	1	

The HP-5993B equipped with PBS software meets the requirements of the Test 9 and can be routinely used for qualitative analyses of complex samples.

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SECTION 3

DISCUSSION OF GENERAL PERFORMANCE

The evaluation was begun on 5 March 1980, and ended on 5 June 1980. Because of other commitments, only 35 of those 66 working days were dedicated to working with the HP-5993B. Approximately 14 days were needed to become familiarized with revision C software and the purge and trap unit. The jet separator and the source were cleaned twice during the evaluation. There was a period of six days of down time, three days each due to blown source filament fuses and a faulty encoder lamp in the disc drive. Validation tests for BFB (Table 6) were obtained in December of 1981 after the DAC was replaced.

Occasionally, some problems were encountered when performing manual background subtractions. For example, the message NO PEAKS would be displayed when the system was instructed to display spectrum (80-74) when spectrum 80 was clearly just at the apex of a small peak and spectrum 74 was clearly on the baseline. Subsequently, if the system was instructed to display spectrum (80-73) or spectrum (81-74) no error message would be displayed and a background corrected mass spectrum would be displayed. This bug has been corrected by HP and does not occur using revision D software.

Once during the evaluation, AUTOTUNE did not perform correctly. After about a minute into the program, the calibration valve closed, yet the program continued running. Since no PFTBA was being leaked into the system, AUTOTUNE could not reach a logical end and had to be halted by typing control S. The master software was reloaded onto the fixed disc and the problem was eliminated.

The problem with the bromine isotope ratio (Table 5) was particularly bothersome. The manufacturer corrected this problem (Table 6) and bromine isotope ratios have been very good since the DAC was replaced.

Overall, the performance of the HP-5993B was more than satisfactory. In the hands of a skilled operator, acceptable performance can be routinely achieved. The HP-5993B is judged acceptable for the GC/MS analysis of environmental samples using methods similar to the EPA approved Methods 624 and 625.

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